

Continuous Volumetric 3D Printing: Xolography in Flow

Lucas Stüwe⁺ Matthias Geiger⁺ Franz Röllgen Thorben Heinze Marcus Reuter Matthias Wessling
Stefan Hecht* John Linkhorst*

L. Stüwe, M. Geiger, F. Röllgen, T. Heinze, M. Wessling, J. Linkhorst

Chemical Process Engineering

RWTH Aachen University

Forckenbeckstr. 51, 52074 Aachen, Germany

* E-mail: john.linkhorst@avt.rwth-aachen.de

M. Reuter

xolo GmbH Volmerstraße 9B, 12489 Berlin, Germany

S. Hecht, M. Wessling

DWI - Leibniz Institute for Interactive Materials

Forckenbeckstr. 50, 52074 Aachen, Germany

S. Hecht

Department of Chemistry

Humboldt-Universität zu Berlin

Brook-Taylor-Str. 2, 12489 Berlin, Germany

* E-mail: sh@hu-berlin.de

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Additive manufacturing techniques continue to improve in resolution, geometrical freedom, and production rates, expanding their application range in research and industry. Most established techniques, however, are based on layer-by-layer polymerization processes, leading to an inherent trade-off between resolution and printing speed. Volumetric 3D printing enables the polymerization of freely defined volumes allowing the fabrication of complex geometries at drastically increased production rates and high resolutions, marking the next chapter in light-based additive manufacturing. This work advances the volumetric 3D printing technique *xolography* to a continuous process. Dual-color photopolymerization is performed in a continuously flowing resin, inside a tailored flow cell. Supported by simulations, the flow profile in the printing area is flattened, and resin velocities at the flow cell walls are increased to minimize unwanted polymerization via laser sheet-induced curing. Various objects are printed continuously and true to shape with smooth surfaces. Parallel object printing paves the way for up-scaling the continuous production, currently reaching production rates up to $1.75 \text{ mm}^3 \text{ s}^{-1}$ for the presented flow cell. Xolography in flow provides a new opportunity for scaling up volumetric 3D printing with the potential to resolve the trade-off between high production rates and high resolution in light-based additive manufacturing.

1 Introduction

Additive manufacturing (AM) is known for its tremendous potential to redefine product fabrication. It opens up vast new applications and opportunities in research, [1,2] ranging from wastewater treatment, [3] the fashion industry, [4] and microfluidics [5] to the fabrication of implants in regenerative medicine, and building blocks for scaffolds in tissue engineering. [6] In the latter, millions of building blocks are required to build a modular scaffold with locally controllable porosity allowing cell interpenetration and nutrient supply. Up to now, high throughput fabrication of this type of building block is only possible by e.g. in-mold polymerization (PRINT) [7] and stop-flow lithography. [8] Both methods are not able to fabricate building blocks with sufficient geometric complexity, i.e., inner and outer structure. An AM technique with continuous production could close this gap.

From the various AM techniques, vat polymerization stands out with high resolution and fine surface finish. [1] The two most common approaches are Stereolithography (SLA) and Digital Light Projection (DLP) printing, achieving printing resolutions up to $75 \mu\text{m}$ and 600 nm , respectively. [9] SLA and DLP are sequential approaches based on layer-by-layer build-up, which necessitates support structures for complex hollow features and overhangs. Furthermore, a trade-off between high resolution and printing speed has to be made. These constraints limit their potential for applications in tissue biofabrication [10]

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⁺These authors contributed equally to this work.

An AM technique that overcomes the limitations on quality and geometry inherent to SLA and DLP is direct laser writing (DLW), based on the principle of two-photon polymerization. This sequential approach is based on voxel-wise polymerization, achieving resolutions of up to 100 nm. However, resolution and production rate are intrinsically coupled as high resolution (i.e., small voxel size) invariably leads to low production rates. [12] While there are approaches to increase the throughput of the DLW process by parallelization, [13] optimization of scanning movements, [14] dynamic tuning of the voxel size, [15] or printing in a moving resin via horizontal [16,17] and vertical flow lithography, [18–20] the limitations of sequential polymerizations remain. These constraints make DLW an attractive technique for specific applications requiring high resolution, such as microfluidics, [21] regenerative medicine, [12] and optics, [22] but limit its use for applications requiring high throughput fabrication.

Continuous vat polymerization techniques, in contrast, do not rely on layer-wise or voxel-wise polymerization, thus improving surface quality and printing speed. Continuous liquid interface production (CLIP), a pioneer in step-less 3D printing, is based on the DLP approach. An image sequence is projected into the vat, while the build-platform is pulled up. An oxygen-permeable surface creates an inhibition zone in the vat, allowing a uniform pulling up of the printed object from the resin-filled vat. At high framerates of the projected images, the printed volume is polymerized continuously in an essentially layer-less manner. [23] The CLIP method was recently improved by adding a photoinhibitor to the process. By creating the inhibition zone via an interplay of a photoinitiator and photoinhibitor, which are activated by different wavelengths, higher resolution and thicker inhibition zones have been achieved, allowing for more viscous resins. [24] Build rates of up to 100 L h⁻¹ [25] and resolutions of 4.5 μm are reported for CLIP. [26] However, CLIP is limited to low viscosity resins, which limits the material choice and complicates biodegradability. [6] In addition, CLIP requires support structures for complex-shaped objects and, at high resolutions, has to abandon the uniform pulling up of the printed object.

Volumetric 3D printing is considered the next step toward rapid and continuous AM with high resolution and printing speed. It abandons the conventional sequential approach of layer-wise fabrication in favor of directly polymerizing a defined resin volume with arbitrary geometry. It thus permits the creation of geometrically complex objects without support structures at unprecedented printing rates. [27] Printing viscous resins with high molecular weight, not suitable for high print resolutions in SLA and DLP processes, could lead to improved mechanical stability and biodegradability. [6] The volumetric 3D printing methods reported in literature are either based on holographic approaches [27,28] or a combination of photomask lithography and dual-color polymerization (DCP), [29,30] achieving resolutions beyond the diffraction limit. [31]

In computed axial lithography (CAL), the most prominent holographic approach, a set of 2D projections of the desired object are projected into a transparent and rotating liquid build volume, allowing the synthesis of arbitrary geometries. [32] The achievable resolution was improved from 300 μm to 80 μm by including an optical feedback system for subsequent prints. [33] Further research on CAL enabled volumetric 3D printing of ceramics [34] and light-scattering resins, [35] the integration of mechanical property gradients via DCP, [36] and in-situ 3D metrology [37] of solidified objects. Recently, Toombs et al. presented a micro-CAL approach to manufacture silica glass with a resolution of 50 μm by using a photopolymer-silica nanocomposite as resin. [38] Debinding and sintering of the printed nanocomposite resulted in 3D microfluidic flow channels with a diameter of 150 μm in fused silica. CAL holds great promise as a volumetric AM method, allowing the fabrication of objects at high rates and resolution. Still, due to the rotating build volume, the process is limited to batch fabrication, following a sequence of preparation, printing, object removal, cleaning, and post-processing.

Xolography is a rapid volumetric 3D printing method that uses DCP for precise volumetric curing via photoswitchable photoinitiators. Light of the first wavelength switches the dual-color photoinitiator from an initial dormant to a latent state. Upon illumination with light of the second wavelength, polymerization is initiated. Thus, polymerization only occurs at the intersection of lights of the two wavelengths. The xube, a 3D printer developed on this operating principle, projects a thin light sheet of the first wavelength into the resin, activating the photoinitiator to its latent state. The desired object geometry is projected with the second wavelength onto this light sheet, initiating polymerization. By continuously moving a

resin-filled cuvette through the light sheet while projecting a sequence of images, complex 3D geometries can be produced in seconds to minutes at volume generation rates of up to $55 \text{ mm}^3 \text{ s}^{-1}$ and resolutions of up to $25 \mu\text{m}$ in the x-y direction and $50 \mu\text{m}$ in the z-direction. [39] Xolography holds the potential to allow fabricating objects with resolution in the double-digit micron range at a concurrent high production rate.

This paper presents a *continuous* volumetric 3D printing approach based on the principle of xolography. Instead of moving a resin-filled cuvette, the resin flows vertically through the light sheet, providing the necessary movement in the z-direction. The second wavelength for DCP is projected onto the light sheet from above, allowing to continuously polymerize the flowing liquid. The flow cell was designed with computer aided design (CAD) and validated with computational fluid dynamics (CFD) simulations to visualize and tailor the resin flow profile. Flow shaping weirs in the flow cell's downstream flatten the flow profile in the printing regime. Two additional side inlets reduce the resin's residence time in the flow cell's margins to prevent unwanted resin curing.

Augmenting xolography into a continuous process offers new possibilities for up-scaling through parallelization and automation of the printing process. Xolography in flow fabricates true-to-shape objects with smooth surfaces and currently reaches fabrication rates of $1.75 \text{ mm}^3 \text{ s}^{-1}$. As a unique continuous fabrication method for complex-shaped objects in the micrometer range, xolography in flow is a promising AM process, for, e.g., particle fabrication for tissue engineering applications, where a large amount of micron-sized building blocks is required to facilitate particle-cell interactions in the scaffold.

2 Results and Discussion

2.1 FlowXube and concept of xolography in flow

Xolography leverages DCP to confine polymerization to a freely defined volume of resin. The photoswitchable photoinitiator used for xolography allows a two-step polymerization mechanism. Upon irradiation with light in the UV spectrum, the dual-color photoinitiator is activated by switching it from its initial dormant spiropyran state to its latent merocyanine state. Illumination of the resin in its latent state with light in the visible spectrum initiates radical polymerization. Thus, the volume to be polymerized is defined through the intersection of UV light, switching the photoinitiator, and visible light, initiating the polymerization. However, the resin's latent state also absorbs light in the UV spectrum. Illumination with UV light at high intensities or for extended periods, and thus higher radiant fluxes, initiates polymerization, even in the absence of light of the second wavelength. This laser sheet-induced curing is an undesired polymerization pathway that undermines the polymerization's confinement to the desired volume.

In xolography, the first wavelength is implemented as a static light sheet. This light sheet spans an x-y plane in which the resin is switched to its latent state. The second wavelength is projected onto the light sheet, defining the x-y confinement of the polymerized volume. [39]

The established implementation of xolography, the *xube* (xolo GmbH), uses a resin-filled cuvette as printing volume. This cuvette is moved along the z-axis through the light sheet. While the cuvette is moved through the light sheet, the projector plays a high-resolution printing movie, a sequence of cross-sectional images of the object to be printed. By synchronizing the frequency of the image sequence to the cuvette's movement, the object is polymerized along its z-axis inside the resin volume.

To transform this process into a continuous one, the movement of the cuvette is replaced by a flowing resin. We built a flow cell to control the resin flow and pump the resin through the light sheet (**Figure 1**). Instead of moving the cuvette, which limits the build volume to the size of the cuvette, the resin flows from top to bottom through the light sheet and facilitates the necessary displacement in the z-direction. This enables an infinite build volume and a continuous process. Furthermore, printed objects are removed from the build volume with the resin flow and can be cleaned and post-processed without interrupting the next object's print. In reference to the established printer named *xube*, we refer to this configuration as the *FlowXube*.

The resin flow inside the cell is governed by laminar flow ($\text{Re} \ll 1$), characterized by smooth streamlines and the absence of turbulence and vorticity. Laminar flow is critical for in-flow printing, as stable and

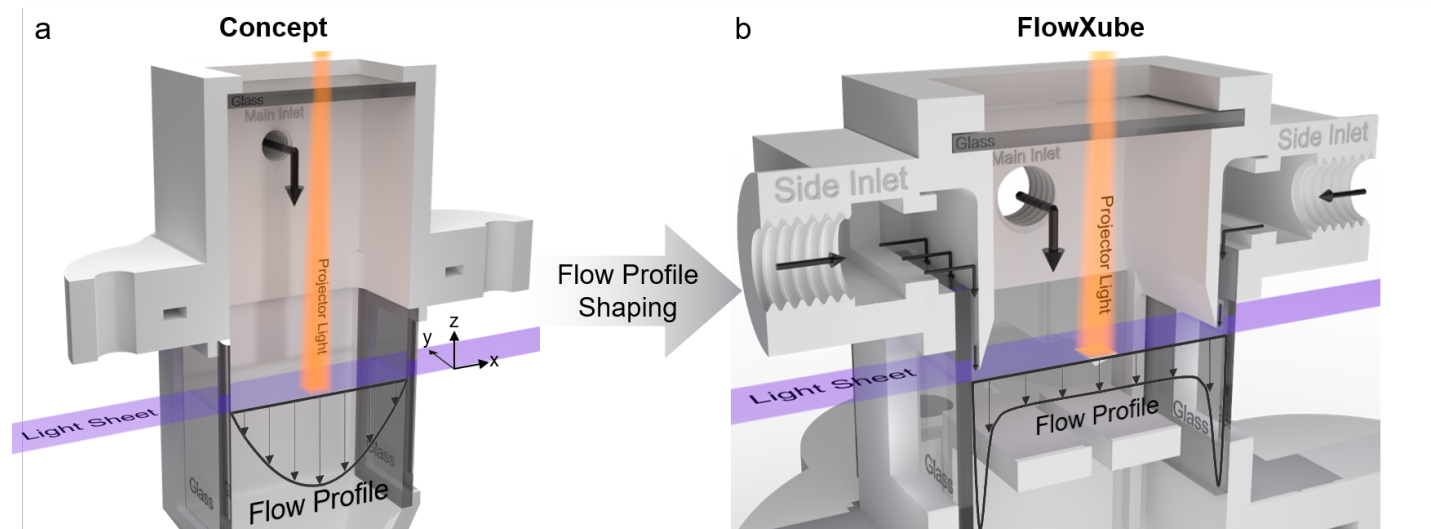


Figure 1: **Concept of xolography in flow and flow shaping in the designed flow cell shown in full section.** (a) Xolography in flow makes use of resin flow to continuously remove the printed objects from the printing area and supply new resin from the top. The printing area is defined by the intersection of the horizontal UV light sheet and the projector light from above. (b) The FlowXube's cell with two side inlets and flow shaping weirs in the downstream is designed to prevent unwanted laser sheet-induced curing in the cell's margins and to flatten the flow profile in the central printing area for homogeneous in-flow printing.

predictable flow conditions with negligible in-plane (x-y) flow velocity are needed to prevent distortion of the printed objects. In a confined space, laminar flow results in a parabolic flow profile with flow velocities being highest in the middle of the chamber and zero at its margins due to the no-slip condition (Figure 1a). These low flow velocities in the cell's margins lead to high residence times of the resin inside the UV-light sheet. The increased radiant flux received by the resin causes laser sheet-induced curing at the glass window near the UV light source. To combat this unwanted effect, we customized the flow cell and incorporated two additional side inlets to shape the flow profile such that flow velocities at the critical margins are high and UV curing is minimized (Figure 1b).

The Flow Cell

The flow cell is a reflectionally symmetric cuboid with glass windows on top and all four sides. The windows on the sides (y-z plane) allow the light sheet to pass into the cell. The window on top (x-y plane) allows projection of the visible light image onto the light sheet. The two additional windows on the sides (x-z plane) are used for in-situ monitoring of the printing process. The resin flows through the flow cell from top to bottom, away from the projector. Thus, shadowing and scattering the projector's image by printed objects is prevented. The resin is delivered through two main inlets close to the top of the cell and two narrow side inlets above the side windows (Figure 1b). The side inlets cause higher flow velocities along the cell's margin, thereby reducing the residence time of the resin and minimizing unwanted laser sheet-induced curing. Printed objects and remaining resin are flushed out through an outlet at the bottom of the cell.

2.2 Flow profile design

The resin's viscosity, the flow cell's size and the applied flow rates result in a highly laminar flow inside the cell. The absence of turbulence and vorticity is ideal for flow printing, as the lateral velocity in the x-y plane, orthogonal to the main flow direction, is very low, minimizing undesired movements of the objects during printing. However, a parabolic flow profile would form without constructional modifications, as shown in Figure 1a. To realize xolography in flow, the flow profile has to fulfill two requirements. First, high flow velocities in the cell's margin are needed to reduce resin exposure times and to minimize

laser sheet-induced curing. Second, the flow velocities need to be equal over the printing area, while lateral flows in the printing plane are avoided to prevent object distortion during the printing process. The flow cell is symmetric along the x and y-axis, resulting in a symmetrical flow profile in the cell. The superposition of the resin flow through the four inlets and the inclusion of flow shaping weirs in the downstream result in an even velocity distribution in the center of the cell. Close to the glass slides at the cell's margin, the flow velocity sharply increases, due to the flow through the side inlets. The flow profile obtained from CFD simulations, shown in **Figure 2a**, demonstrates the fulfillment of both requirements, the homogeneous velocity in the cell's center and high velocities in the margins. Since xolography is initiated at the intersection of both wavelengths, all CFD simulations are evaluated in the light sheet, as this plane defines the location of the active printing area. The area available for printing is limited by the projection size of the visible light and the diverging light sheet. The light sheet is focused by converging lenses to a waist of 20 μm in the center of the flow cell and widens towards the cell's margins. As a wider light sheet reduces the z-resolution, we define a width in the x-direction wherein the light sheet divergence is below 10% to maintain high resolution in the z-direction. This restriction results in a printing area with a width of 3 mm in the x-direction with a light sheet width ranging from 20 μm in the middle to 22 μm at the margins. To emphasize the printing area's location in x-direction, it is highlighted in orange in Figure 2a and b. In the y-direction, the printing area is limited by the projection size of 10 mm. This results in a printing area of 30 mm².

The distinctness of the characteristic zones of the flow in the light sheet strongly depends on the distance d from the side inlets in the z-direction. Flow velocities at the cell's margins are highest at a small value for d , just below the side inlets (Figure 2a). With increasing distance from the side inlets, the flow returns to the parabolic flow profile characteristic for confined laminar flow. Therefore, the light sheet, and thus the printing area, should be as close as possible to the side inlets. As the light sheet is manually positioned and illumination has to be unobstructed by the inlets, the light sheet is positioned $d = 1$ mm below the side inlets.

Besides the distance d , the flow profile can be influenced by adjusting the inlet ratio r of the volume flow of the side inlets $\dot{V}_{side}$ to the volume flow of the main inlets $\dot{V}_{main}$ (Figure 2b). Increasing the inlet ratio leads to higher resin velocities at the cell's margins, which in turn reduces laser sheet-induced curing. However, as the inlet ratio is increased, the velocity distribution in the printing area becomes less homogeneous, leading to possible object distortion. In the given cell geometry, for an inlet ratio of $r = 10$, the deviation of the resin velocity in the printing area increases up to 11.2%, while for a ratio of 5, 3 and 1 the deviation is 5.9%, 3.5% and 0.9%, respectively. Moreover, high flow rates through the side inlets cause in-plane flows from the margin toward the center (x and y-direction). Increasing the flow rate through the side inlets increases these lateral flows, which adversely affect print quality (Supporting Information for further details). Besides causing an inhomogeneous flow profile, high flow velocities outside the printing area lead to higher amounts of resin unavailable for printing, which must be either recycled or discarded. For the printed objects presented in this work, an inlet ratio of 5 was chosen as it provided a good compromise between minimizing laser sheet-induced curing for a maximum number of subsequent prints and achieving homogeneous flow condition in the printing area for undistorted objects. Two strategies could be applied to optimize flow conditions and further increase the print quality of xolography in flow. As the flow profile for $d = 0.5$ mm in Figure 2a demonstrates, increased manufacturing precision of the cell and more precise positioning in the light sheet will create a more beneficial flow profile rendering the printing area larger. The second option is a software correction that considers the velocity deviations in the peripheral regions. In this case, complete utilization of the projection surface for maximum up-scaling could be possible. However, a decrease in resolution in the outer regions has to be taken into account.

Critical Resin Velocity

Through UV irradiation, the photoinitiator intentionally switches to its latent state. However, prolonged exposure or high intensity, and thus a higher radiant flux received by the resin, can activate an undesired polymerization pathway. For laser sheet-induced curing to occur, the radiant energy density per volume

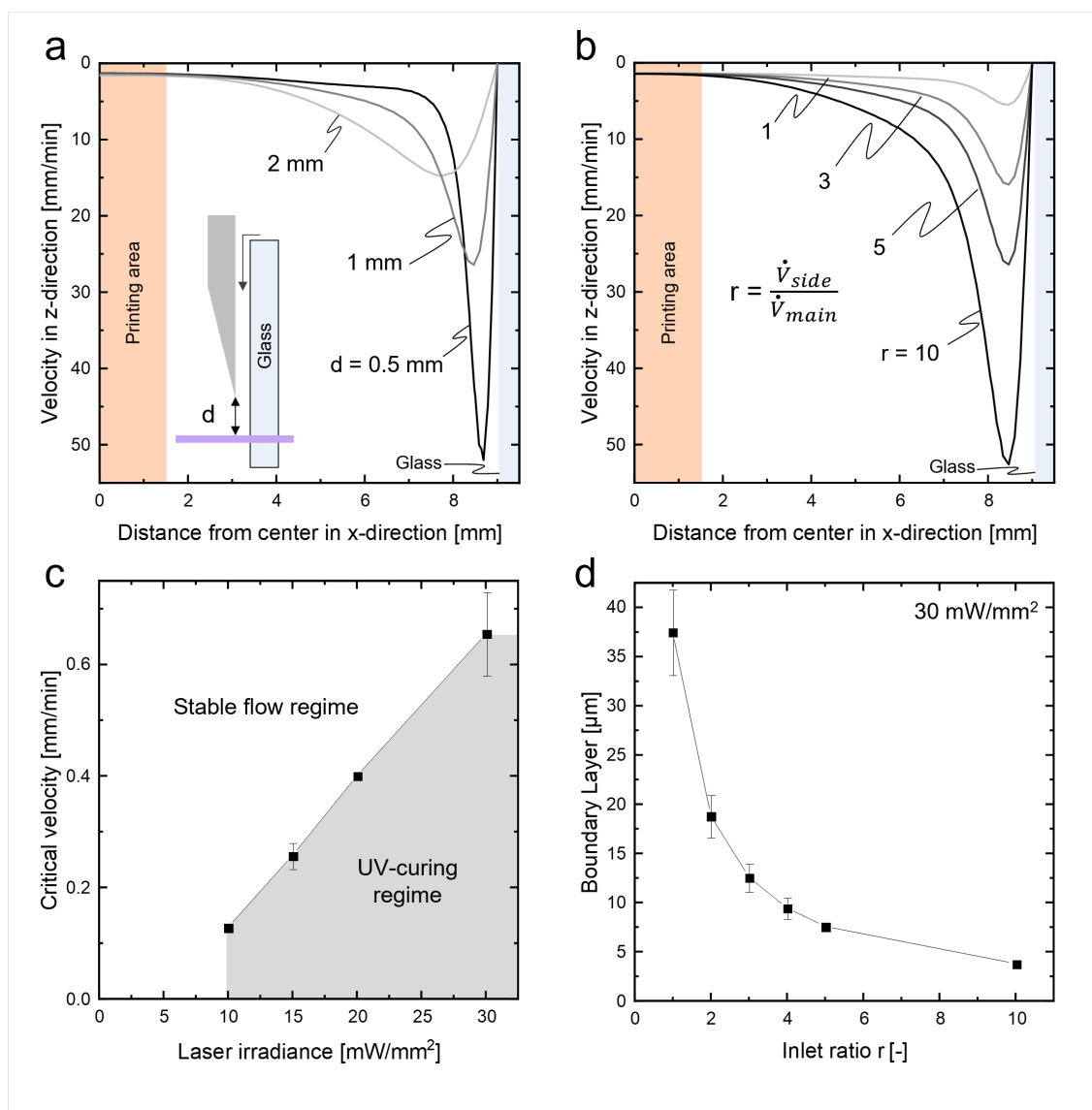


Figure 2: **Parameter space for xolography in flow.** (a) Influence of the distance d between light sheet and side inlet on the flow profile in the z-direction obtained from CFD simulations for an inlet ratio of 5. (b) CFD simulated flow profile for different inlet volume flow ratios at a distance of $d=1$ mm. The orange regions depict the printing area in the x-direction wherein the divergence of the light sheet width of $20 \mu\text{m}$ is limited to 10%. (c) Critical flow velocity for laser sheet-induced curing and corresponding regime for stable printing without unwanted curing ($n=3$). (d) Boundary layer thickness at the flow cell's margin for different inlet ratios based on CFD simulations at $30 \text{ mW}/\text{mm}^2$ and $d=1$ mm distance between light sheet and side inlet based on the critical velocity from (c).

element of resin has to exceed a polymerization threshold. We determined the corresponding critical velocity to further characterize the circumstances of laser sheet-induced curing. First, we determined a critical residence time for different laser irradiances marking the occurrence of laser sheet-induced curing. Assuming a constant velocity in the printing area, a critical velocity is calculated (Figure 2c). With increasing laser irradiance, the critical velocity increases, creating a lower bound for the velocity to avoid laser sheet-induced curing. In the central zone, the resin flow exceeds the critical velocity for all inlet ratios. For the cell's margin, we define a boundary layer at risk of laser sheet-induced curing as the area at the cell's margin in which the flow velocity is below the critical velocity. The boundary layer thickness for different inlet ratios based on the flow profiles obtained from the simulations is shown in Figure 2d. Despite the reduction of the boundary layer thickness through active flow profile shaping, a certain margin of resin remains below the critical velocity due to the no-slip condition. Here, oxygen diffusing in from the adjacent more mobile layers quenches photoinitiator radicals activated by the UV light. In a sufficiently thin boundary layer, laser sheet-induced curing would be prevented by oxygen inhibition. However, increasing the side inlets flow rates further to reduce the boundary layer thickness leads to more inhomogeneous and lateral flows in the printing zone. Thus, laser sheet-induced curing at the cell's windows was minimized but not fully prevented. An indicator for the onset of laser sheet-induced curing on the glass windows is the scattering of laser light. Cured resin stuck on the glass slides is detrimental to the focus of the light sheet. Moreover, it absorbs photons required for switching the photoinitiator to its latent state in the printing area. Both effects lower printing quality and thus should be minimized by further reducing the boundary layer. In the experiments, however, more than 20 consecutive prints could be performed before laser sheet-induced curing at the lateral glass slides affected printing quality.

- Based on CFD simulations, we confined the parameter space for xolography in flow consisting of the light sheet's position, the inlet ratio, and the laser power. A sweet spot between a uniform flow profile in the printing area for high printing resolutions and a thin boundary layer for reducing laser sheet-induced curing in the cell's margin was found.

2.3 Print accuracy

With the parameter space for xolography in flow set, cuboids and pyramids were printed to determine accuracy of the printed shapes, surface quality and minimum features sizes. Analysis of the particles with scanning electron microscopy (Figure 3 c,f,i) revealed that the process produced the intended shapes accurately. Non-ideal flow of the resin in the printing area, caused by e.g. bubbles, inhomogeneous inflow, or laser sheet-induced curing in the cell's margins, would have caused distortion of the particles. Therefore, the shape fidelity of the printed particles proves the homogeneity of the flow in the printing area, in agreement with the simulations. In xolography in flow, the height of a polymerized volume depends on the resin's flow velocity and the duration of illumination. Based on CFD simulations, the playback rate of the projected image sequence was synchronized to the resin velocity in the printing area. As a mismatch of flow velocity and playback rate would have lead to deviations between desired and printed height, the shape fidelity of the particles also proves successful synchronization. The mean edge length of six consecutively printed cuboids (Figure 3a-c) was $605 \mu\text{m} \pm 36 \mu\text{m}$. As the projected shape had an edge length of $1000 \mu\text{m}$, the printed cubes are subject to a homogeneous shrinkage of 39.5%. The printed square pyramids in Figures 3g-i demonstrate consistency with the 3D model. However, shrinkage of up to 56% between a designed edge length of 1 mm and printed edge length was observed. The tilted surfaces of the pyramid demonstrate the layer-less appearance of objects printed with xolography in flow. Even though the minimum lateral resolution provided by the projector is $5 \mu\text{m}$, the tilted surfaces are smooth with no discernible layers or steps. The layer-less appearance is independent of the surfaces orientation during the print. Material volume shrinkage is a well-discussed phenomenon in the literature, attributed to factors such as shortening of inter-molecular distances during (post-)polymerization [40], micro-void formation [41], and incomplete resin polymerization [42]. Some (meth)acrylate-based monomers have been reported to exhibit volume shrinkage above 20% [43]. For xolography in flow, we assume that a large amount of uncured resin is washed out in the post-processing, further facilitated by the

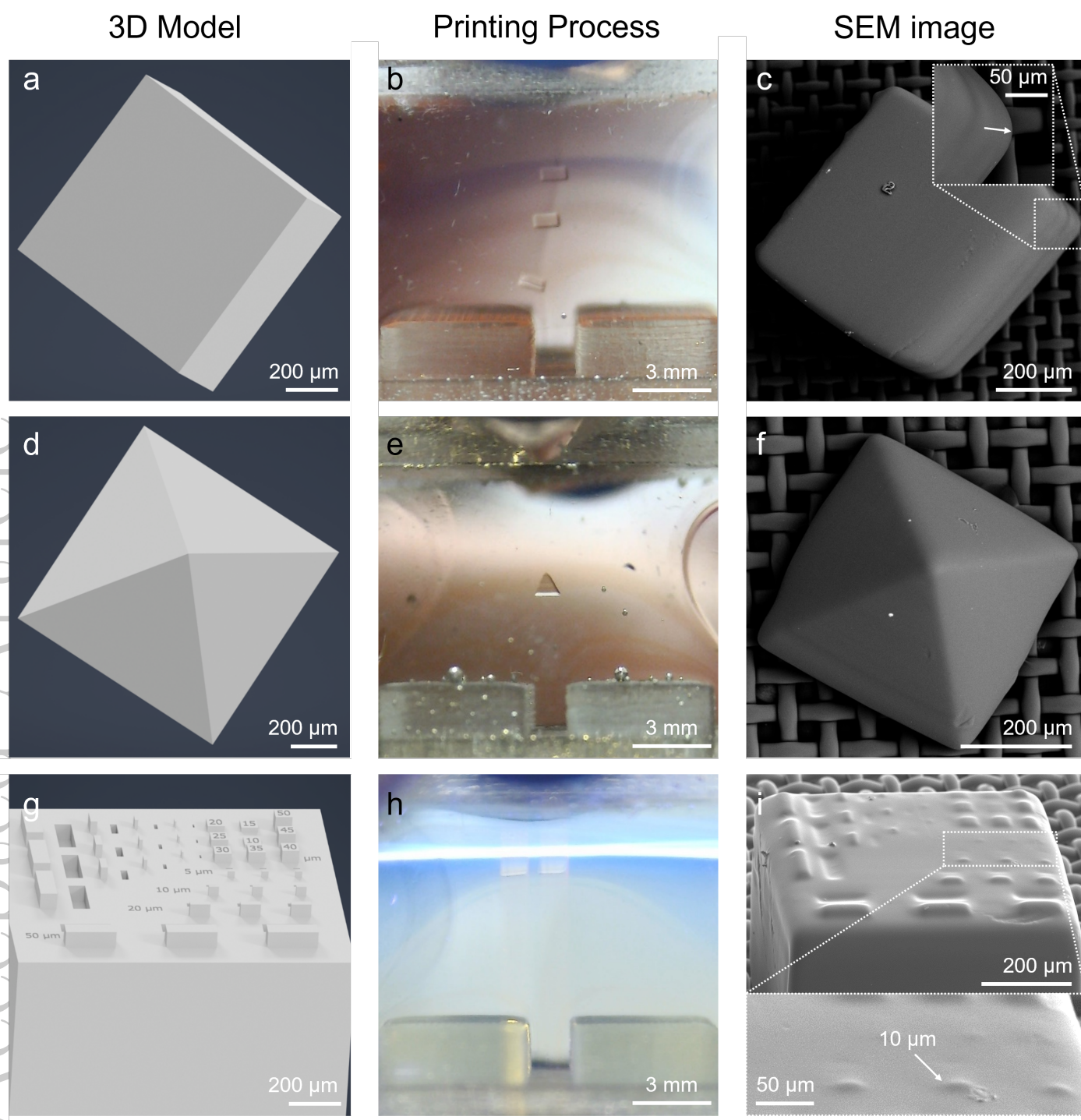


Figure 3: Print accuracy of xolography in flow. 3D models (a,d,g) are printed in the flow cell, which allows in-situ observation of the print (b,e,h). The SEM images (c,f,i) show the shape fidelity of the objects with smooth surfaces proving the homogeneity of the flow in the printing area. Note that the blue and yellow color streaks in (b,e,h) show the photoinitiator in the latent state during the illumination process of resin volume. (i) illustrates the first recognizable features of the 10 μm row.

high surface-to-volume ratio of the printed objects leading to the formation of micro-voids throughout the particles and subsequently to the high degree of shrinkage observed. Further on, we determined a minimum recognizable feature size for xolography in flow to prove reasonable focusing of the projector light in the light sheet and to demonstrate the possible potential. Bars with decreasing width (50, 20, 10 and 5 μm) and rectangular features with altering height (in 5 μm increments, ranging from 50 to 10 μm) were printed on top of a cuboid. Upon examination of the SEM image presented in Figure 3i, the smallest printable and recognizable feature sizes were found in the 10 μm row in both the x and y directions. The rectangular features in the z-direction could be identified down to a height of 25 μm . The achievable minimum feature sizes for xolography in flow, however, is impaired by the fact that all objects feature rounded corners and edges due to an under-curing of small features as described by Orth et. al. for other volumetric 3D printing approaches. [44] Adjacent surfaces have a filleted appearance with a radius of approximately 23 μm (see Figure 3c). This smoothing results in the superior surface quality, however, it also compromises the shape fidelity of the printed bars with an intended thickness of 10 μm .

2.4 Scale-up

The key advantage of continuous printing methods is the ease of scaling up the processes. For xolography in flow, up-scaling is limited by the available printing area and the maximum velocity of the resin in this area. The printing area for xolography in flow is limited in the x-direction by the length over which the light sheet width is within acceptable divergence from its 20 μm waist, and in the y-direction by the size of the projection area. With a length in the x-direction of 3 mm and a projection width in the y-direction of 10 mm, the printing area yields 30 mm^2 at maximum resolution in the z-direction. The printing area could be further increased toward the cell's margin, which would reduce z-resolution. As the width for projection is 17 mm in the x-direction, the maximal printing area when neglecting light sheet width is 170 mm^2 . To demonstrate the capability of the FlowXube for parallel prints, we printed an array of 5x17 rods with designed diameter and length of 200 μm and 1000 μm , respectively, spread over the full printing area (**Figure 4a**) multiple times consecutively (Figure 4b). The corresponding SEM images of the obtained rods (Figure 4c) reveal a mean rod diameter of $107.0 \mu\text{m} \pm 16.1 \mu\text{m}$ and a mean rod length of $525.0 \mu\text{m} \pm 25.4 \mu\text{m}$ ($n=23$), proving reasonably constant printing conditions over the entire printing area. However, the rods are subject to homogeneous shrinkage in both, diameter and length, of approximately 47%.

To determine the minimum distance required between two objects, we printed a rectangular cuboid of 2.9x1x1 mm carrying fins of decreasing distance (Figures 4d,e). To prevent curing in between adjacent objects and ensure a distinction between objects and their corresponding radii, a minimum separation distance of at least twice the radius of 23 μm is required. Additionally, a printed feature has to resemble the designed structure. In the SEM images (Figure 4f) a clear distinction between two fins can be made for distances of 80 μm and greater. Thus, multiple objects can be printed in parallel, when a minimum object distance of 80 μm is maintained. With further improvements regarding projector focusing or by grayscaleing of the projector increasing local irradiance of small features, even denser packing of objects might be possible.

The resin velocity in the printing area is the second factor influencing the scale-up of xolography in flow. An increase in flow rate leads to higher fabrication rates but also increases the minimum feature size in z-direction. To realize higher flow velocities, the laser power of the UV-light sheet needs to be increased to maintain the necessary radiant flux received by the resin in the light sheet for switching the photoinitiator to its latent state, as the resin's exposure time is reduced. In concluding experiments, we achieved a maximum resin velocity of 3.5 mm min^{-1} while maintaining stable printing conditions. The maximum resin velocity is limited by the irradiance of the visible light supplied by the projector. Further increasing the resin velocity leads to incomplete curing, as the exposure to the second wavelength is insufficient for polymerization. In order to maintain the printing conditions and to keep the equilibrium between the initial dormant and latent state of the photoinitiator constant, a linear increase of the projector's irradiance would be necessary in addition to the linearly increase in resin velocity and in light sheet irradiance. However, a projector with higher irradiance to increase the printing rate and further

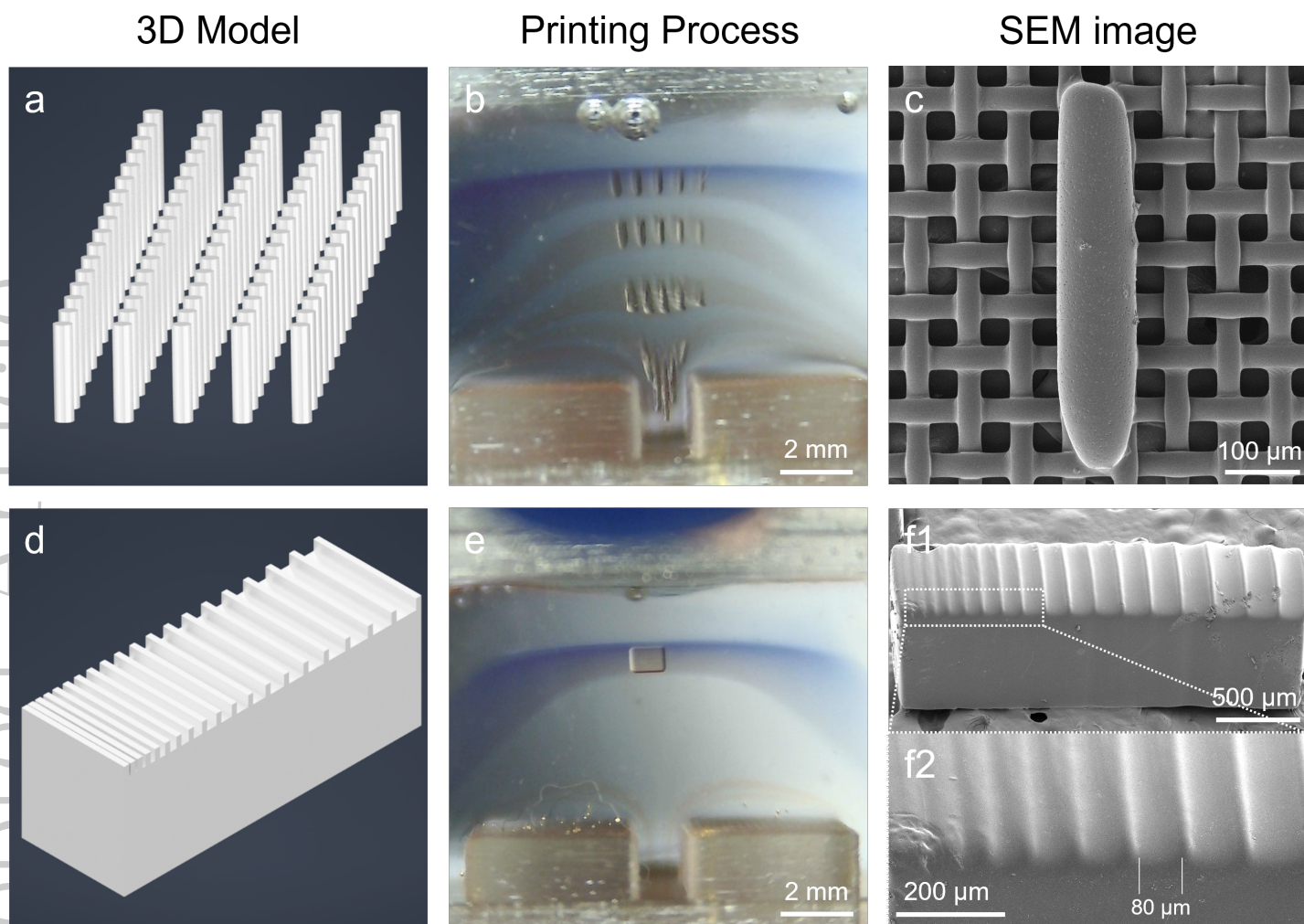


Figure 4: Up-scaling xolography in flow. (a) 3D model of 5x17 rod array, (b) 5 consecutive prints of the arrays, utilizing the full printing area. (c) SEM image showing the actual shape of a single printed rod after post-processing on a cell strainer mesh. (d) 3D model of a cuboid with fins of varying distance to identify the minimum object distance, (e) corresponding image of the printing process, and (f) SEM analysis to determine the minimum object distance to be 80 μm .

boost fabrication speed and throughput is currently unavailable.

The prints in Figure 4 clearly demonstrate the up-scaling feasibility of the first continuous volumetric 3D printing process. The maximum resin velocity of 3.5 mm min^{-1} combined with complete utilization of the printing area of 30 mm^2 at the minimum light sheet width leads to a maximum fabrication rate of $1.75 \text{ mm}^3 \text{ s}^{-1}$ for xolography in flow.

3 Conclusion

In this work, we present xolography in flow as the first continuous and volumetric 3D-printing method based on the principle of dual-color photopolymerization. The flow cell presented here shapes the flow profile of the flowing resin to allow uniform continuous printing and minimize the detrimental laser sheet-induced curing. The realization of a continuous volumetric printing method enables the versatile fabrication of various building blocks, e.g., for tissue engineering, at high throughput and high resolution. First printed objects are true to shape and show smooth surfaces at minimum recognizable feature sizes of about $10 \mu\text{m}$ in the x/y and $25 \mu\text{m}$ in the z-direction. The features are compromised by a radius of approx. $23 \mu\text{m}$ appearing on every edge of an object. For up-scaling, the tailored flow conditions in the flow cell permit parallel printing of multiple objects along the entire printing area at a minimum object distance of $80 \mu\text{m}$ and at maximum fabrication rates of $1.75 \text{ mm}^3 \text{ s}^{-1}$.

The current resolution and volume generation rates achieved in this work do not yet represent the limits of the xolography principle. Further improvements in the focusing of the projector, the positioning of the flow cell in the light sheet, and the adaptation of the light sheet optics to the flow cell's width could bring the realized resolution closer towards the resolution of the projector. Grayscale of the projector might even result in resolutions below the theoretical limit of the projector by increasing local irradiance of small features. Due to the utilization of xolography, further up-scaling is only limited by the focal depth of the light sheet. Thus, the printing area could be increased by a wider light sheet (y-direction) and, at reduced z-resolution, by a wider focus depth of the light sheet. In addition, the entire projection area could be used when implementing a software-based correction of the projection images. Furthermore, the implementation of a projector with higher irradiance would establish constant printing conditions at elevated resin velocities. To further reduce or completely prevent laser sheet-induced curing, an oxygen inhibition layer at the cell margins could be created using oxygen-permeable glass, as already applied in CLIP. [23, 25, 26] Additionally, improving the photoswitchable photoinitiator to reduce absorption of light in the UV spectrum of the resin's latent state could alleviate this issue. In summary, xolography in flow constitutes a highly flexible approach, which can be scaled up further with relatively modest improvements and holds the potential to achieve unprecedented volume generation rates of geometrically complex objects with high resolutions and surface quality.

4 Experimental Section

The FlowXube:

Xolography in flow was performed with a prototype of the 3D-printer xube (xolo GmbH), here referred to as the FlowXube. The FlowXube's projector features UHD resolution of 3840×2160 pixel, resulting in a projection area of $17 \times 10 \text{ mm}$ with a resolution of approximately $5 \mu\text{m}$ in x and y. The light source of the projector emits light at a peak wavelength of approximately 585 nm with an irradiance of 227 mW cm^{-2} . The laser sheet is produced by two violet diode lasers (HL40053MG, Ushio) at a wavelength of 405 nm and a maximum output power of 500 mW . Two converging lenses focus the light sheet to a waist of $20 \mu\text{m}$. Based on the calculations in Regehy *et al.*, [39] the light sheet symmetrically widens by 10% to $22 \mu\text{m}$ over a width of 1.5 mm .

Photoresin:

The resin used for printing was supplied by xolo GmbH and is a $>95\%$ urethane methacrylate based resin including the dual-color photoinitiator XC471 (xolo GmbH). The dual color photoinitiator is a

benzophenone type II photoinitiator that is integrated into a spiropyran photoswitch. The resin contains a co-initiator for radical polymerization and pentaerythritol tetraacrylate to tailor the photoswitch's thermal relaxation from the latent to the initial dormant state. Further information about the photoinitiator and its preparation can be found in Regehley et al. [39] For precise CFD simulations of the flow conditions in the flow cell, material data of the resin are required. The resin's density ρ was determined to 1.1006 g cm^{-3} by Cemprom DMA 46 (Anton Paar). The viscosity η of 7.9 Pa s was measured via a cone and plate viscometer Physica MCR 501 (Anton Paar). To determine the critical residence time, a resin-filled cuvette was exposed to the laser sheet in the absence of visible light from the projector. The laser sheet's irradiance was varied from 10 to 30 mW mm^{-2} . The time until the onset of polymerization was measured. Combined with the light sheet width of $20 \mu\text{m}$, the critical velocity is calculated.

Cell design and assembly:

The flow cell was designed in Autodesk Inventor 2023 (Autodesk). The flow cell was printed on a polyjet printer (Objet Eden 260V, Stratasys) from VeroClear (Stratasys) material. It consists of two lids for the side inlets, a top and a bottom part. The lids are glued to the top part, which is then fixed to the bottom part with screws and sealed with an O-ring. Four glass slides ($26 \times 76 \times 1 \text{ mm}$, Avantor) were cut to shape and glued into position with UV-curable glue (LOCTITE® AA 3345, Henkel). IQS-push-in fittings were screwed into the cell for the connection to tubes for the supply of resin.

Data pre-processing, flow printing, and post-processing:

The printed objects were created and designed in Autodesk Inventor 2023. The 3D object file was sliced into separate 2D images with a slice thickness of $s = 5 \mu\text{m}$ by ChiTuBox (CBD-Tech). The images were assembled into an ultrahigh-definition black-and-white printing movie with a fixed frame rate by ffmpeg-based software from xolo GmbH. To print accurately sized objects, the frame rate of the printing movie was synchronized with the resin flow rate through the main inlet $\dot{V}_{main}$. For this purpose, we used a correlation factor $F_{corr} = v_{print}/\dot{V}_{main}$, representing the relationship between resin flow rate and resin velocity in the printing area. As the influence of the flow through the side inlets on the printing speed is negligible, F_{corr} is constant for different inlet volume flows. It depends only on the cell's geometry and can be predicted through simulations. For the presented cell, F_{corr} was determined to $17.1 \mu\text{m } \mu\text{L}^{-1}$. The frame rate of the printing movie is the fraction of the resin velocity in the printing area and the height of a single frame, the slicing height. Using the correlation factor, the frame rate for each print was calculated from:

$$f = \frac{v_{print}}{s} = \dot{V}_{main} \cdot \frac{F_{corr}}{s} \quad (1)$$

For in-flow printing, the cell was connected with tubes (polyurethane, $6 \times 4 \text{ mm}$, Sang-A) and filled with resin. Each inlet was connected to a syringe pump (Standard PHD ULTRA™, Harvard Apparatus). The flow rates of the side inlets and the main inlets were kept equal to ensure a symmetrical flow profile.

For the main inlets, the syringe pumps were set to $\dot{V}_{main} = 58.43 \mu\text{L min}^{-1}$. This resulted in a resin velocity of $v_{print} = 1 \text{ mm min}^{-1}$. The flow rate ratio of the main to side inlet was set to $r = 5$, resulting in a side inlet flow rate of $\dot{V}_{side} = 292.15 \mu\text{L min}^{-1}$. The light sheet was set to 20 mW mm^{-2} . After the printing process, the resin containing the printed objects was captured and dissolved by immersion in isopropyl alcohol under mild agitation to keep the printed object in float. After removal of the resin, the object was left to sediment, excess isopropyl alcohol was removed, and a photoinitiator (ITX, Isopropyl-9H-thioxanthene-9-one, Sigma-Aldrich) was added to the solution at a concentration of 5 mg mL^{-1} . The objects were cured with UV light (302 nm) at 0.96 mW cm^{-2} for 6 h , removed from the bath, and left to dry on a cell strainer ($40 \mu\text{m}$, Corning).

Simulations:

To unravel the velocity distribution inside the flow cell, CFD simulations were performed with COMSOL Multiphysics (vers. 6.0, COMSOL AB) for laminar single-phase conditions. The determined resin's density ρ and viscosity η , the width of the flow cell $d_{cell} = 18 \text{ mm}$ and the averaged velocity in the printing area of 13.7 mm min^{-1} are used to estimate a Reynolds number of 0.0006 , proving laminar conditions. The temperature was set to 293.15 K . As the flow cell is symmetric along the x and y axis, a quarter of the flow cell's volume is used for flow simulations.

Analysis:

The printed objects were analyzed by electron microscopy (TM 3030 Plus, Hitachi Europe Limited, and Schottky Field Emission Scanning Electron Microscope SU5000, Hitachi Europe Limited). Further analysis of microscopy images was performed with ImageJ.

Statistical Analysis: Quantitative analyses were performed using Image-J software. Radii and geometric features were obtained from the electron microscopy images and reported as means and standard deviations. Data were analyzed and plotted using Origin software and reported as means and standard deviations. The critical residence time was determined in three different experiments (n=3). The resulting critical velocity is plotted including a standard deviation in error bars for each data point.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of interest

The authors declare no conflict of interest.

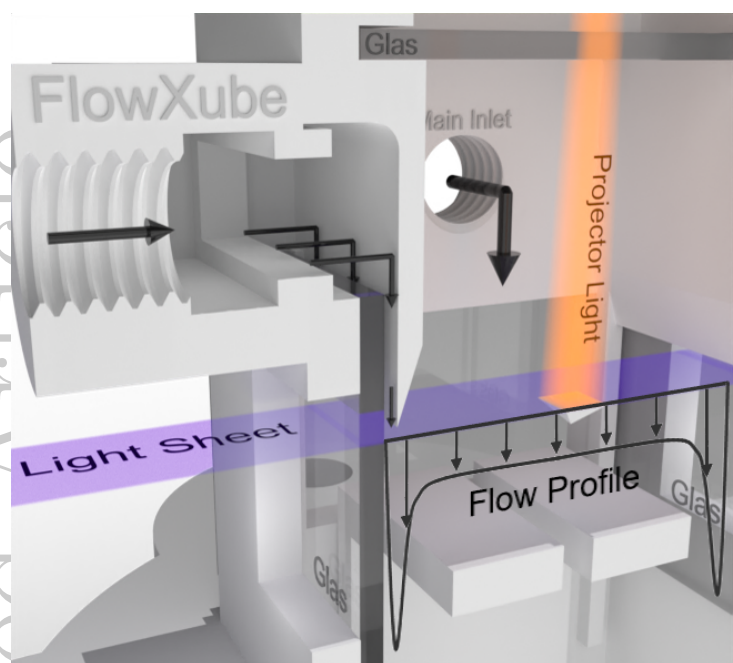
References

- [1] K. L. Sampson, B. Deore, A. Go, M. A. Nayak, A. Orth, M. Gallerneault, P. R. L. Malenfant, C. Paquet, *J. Appl. Polym. Sci.* **2021**, *3*, 9 4304.
- [2] R. Jiang, R. Kleer, F. T. Piller, *Technol. Forecast Soc. Change* **2017**, *117* 84.
- [3] N. H. Mohd Yusoff, L.-R. Irene Teo, S. J. Phang, V.-L. Wong, K. H. Cheah, S.-S. Lim, *J. Chem. Eng.* **2022**, *429* 132311.
- [4] S. Chakraborty, M. C. Biswas, *Compos. Struct.* **2020**, *248* 112562.
- [5] G. Weisgrab, A. Ovsianikov, P. F. Costa, *Adv. Mater. Technol.* **2019**, *4*, 10 1900275.
- [6] Y. Bao, N. Paunović, J.-C. Leroux, *Adv. Funct. Mater.* **2022**, *32*, 15 2109864.
- [7] J. C. Rose, M. Cámara-Torres, K. Rahimi, J. Köhler, M. Möller, L. de Laporte, *Nano letters* **2017**, *17*, 6 3782.
- [8] H. J. M. Wolff, J. Linkhorst, T. Göttlich, J. Savinsky, A. J. D. Krüger, L. de Laporte, M. Wessling, *Lab on a chip* **2020**, *20*, 2 285.
- [9] Q. Ge, Z. Li, Z. Wang, K. Kowsari, W. Zhang, X. He, J. Zhou, N. X. Fang, *Int. J. Extreme Manuf.* **2020**, *2*, 2 022004.
- [10] P. N. Bernal, P. Delrot, D. Loterie, Y. Li, J. Malda, C. Moser, R. Levato, *Adv. Mater.* **2019**, *31*, 42 e1904209.

- [11] D. Rommel, M. Mork, S. Vedaraman, C. Bastard, L. P. B. Guerzoni, Y. Kittel, R. Vinokur, N. Born, T. Haraszti, L. de Laporte, *Advanced science (Weinheim, Baden-Wurttemberg, Germany)* **2022**, *9*, 10 e2103554.
- [12] J. Song, C. Michas, C. S. Chen, A. E. White, M. W. Grinstaff, *Adv. Healthc. Mater.* **2020**, *9*, 1 e1901217.
- [13] S. K. Saha, D. Wang, V. H. Nguyen, Y. Chang, J. S. Oakdale, S.-C. Chen, *Science* **2019**, *366*, 6461 105.
- [14] L. Jonušauskas, D. Gailevičius, S. Rekštytė, T. Baldacchini, S. Juodkasis, M. Malinauskas, *Optics express* **2019**, *27*, 11 15205.
- [15] T. Tičkūnas, D. Paipulas, V. Purlys, *Optical Materials Express* **2020**, *10*, 6 1432.
- [16] S. C. Laza, M. Polo, A. A. R. Neves, R. Cingolani, A. Camposeo, D. Pisignano, *Advanced materials (Deerfield Beach, Fla.)* **2012**, *24*, 10 1304.
- [17] L. A. Shaw, S. Chizari, M. Shusteff, H. Naghsh-Nilchi, D. Di Carlo, J. B. Hopkins, *Opt. Express* **2018**, *26*, 10 13543.
- [18] S. Habasaki, W. C. Lee, S. Yoshida, S. Takeuchi, *Small* **2015**, *11*, 48 6391.
- [19] J. Lölsberg, A. Cinar, D. Felder, G. Linz, S. Djeljadini, M. Wessling, *Small* **2019**, *15*, 33 e1901356.
- [20] A. Lüken, L. Stüwe, S. B. Rauer, J. Oelker, J. Linkhorst, M. Wessling, *Small* **2022**, *18*, 15 e2107508.
- [21] C. Liu, *Microfluid. Nanofluidics* **2010**, *9*, 4-5 923.
- [22] J. Li, P. Fejes, D. Lorensen, B. C. Quirk, P. B. Noble, R. W. Kirk, A. Orth, F. M. Wood, B. C. Gibson, D. D. Sampson, R. A. McLaughlin, *Sci. Rep.* **2018**, *8*, 1 14789.
- [23] J. R. Tumbleston, D. Shirvanyants, N. Ermoshkin, R. Janusiewicz, A. R. Johnson, D. Kelly, K. Chen, R. Pinschmidt, J. P. Rolland, A. Ermoshkin, E. T. Samulski, J. M. DeSimone, *Science* **2015**, *347*, 6228 1349.
- [24] M. P. de Beer, H. L. van der Laan, M. A. Cole, R. J. Whelan, M. A. Burns, T. F. Scott, *Sci. Adv.* **2019**, *5*, 1 eaau8723.
- [25] D. A. Walker, J. L. Hedrick, C. A. Mirkin, *Science* **2019**, *366*, 6463 360.
- [26] K. Hsiao, B. J. Lee, T. Samuelsen, G. Lipkowitz, J. M. Kronenfeld, D. Ilyn, A. Shih, M. T. Dulay, L. Tate, E. S. G. Shaqfeh, J. M. DeSimone, *Sci. Adv.* **2022**, *8*, 46 eabq2846.
- [27] M. Shusteff, A. E. M. Browar, B. E. Kelly, J. Henriksson, T. H. Weisgraber, R. M. Panas, N. X. Fang, C. M. Spadaccini, *Sci. Adv.* **2017**, *3*, 12 eaao5496.
- [28] L. Rodríguez-Pombo, X. Xu, A. Seijo-Rabina, J. J. Ong, C. Alvarez-Lorenzo, C. Rial, D. Nieto, S. Gaisford, A. W. Basit, A. Goyanes, *Addit. Manuf.* **2022**, *52* 102673.
- [29] W. K. Swainson, Method, medium and apparatus for producing three-dimensional figure product, **1977**.
- [30] H. L. van der Laan, M. A. Burns, T. F. Scott, *ACS Macro Lett.* **2019**, *8*, 8 899.
- [31] N. Liaros, J. T. Fourkas, *Opt. Mater. Express* **2019**, *9*, 7 3006.
- [32] B. E. Kelly, I. Bhattacharya, H. Heidari, M. Shusteff, C. M. Spadaccini, H. K. Taylor, *Science* **2019**, *363*, 6431 1075.
- [33] D. Loterie, P. Delrot, C. Moser, *Nat. Commun.* **2020**, *11*, 1 852.

- [34] M. Kollep, G. Konstantinou, J. Madrid-Wolff, A. Boniface, L. Hagelüken, P. V. W. Sasikumar, G. Blugan, P. Delrot, D. Loterie, J. Brugger, C. Moser, *Adv. Eng. Mater.* **2022**, *24*, 7 2101345.
- [35] J. Madrid-Wolff, A. Boniface, D. Loterie, P. Delrot, C. Moser, Light-based volumetric additive manufacturing in scattering resins, URL <http://arxiv.org/pdf/2105.14952v1>.
- [36] B. Wang, E. Engay, P. R. Stubbe, S. Z. Moghaddam, E. Thormann, K. Almdal, A. Islam, Y. Yang, *Nat. Commun.* **2022**, *13*, 1 367.
- [37] A. Orth, K. L. Sampson, Y. Zhang, K. Ting, D. A. van Egmond, K. Laqua, T. Lacelle, D. Webber, D. Fatehi, J. Boisvert, C. Paquet, *Addit. Manuf.* **2022**, *56* 102869.
- [38] J. T. Toombs, M. Luitz, C. C. Cook, S. Jenne, C. C. Li, B. E. Rapp, F. Kotz-Helmer, H. K. Taylor, *Science* **2022**, *376*, 6590 308.
- [39] M. Regehly, Y. Garmshausen, M. Reuter, N. F. König, E. Israel, D. P. Kelly, C.-Y. Chou, K. Koch, B. Asfari, S. Hecht, *Nature* **2020**, *588*, 7839 620.
- [40] J. Jakubiak, L.-A. Linden, *Polimery* **2001**, *46*, 7-8 522.
- [41] Y.-J. Huang, C.-M. Liang, *Polymer* **1996**, *37*, 3 401.
- [42] M. Dewaele, D. Truffier-Boutry, J. Devaux, G. Leloup, *Dental Materials* **2006**, *22*, 4 359.
- [43] Y. Jian, Y. He, T. Jiang, C. Li, W. Yang, J. Nie, *Journal of Polymer Science Part B: Polymer Physics* **2012**, *50*, 13 923.
- [44] A. Orth, D. Webber, Y. Zhang, K. L. Sampson, H. W. de Haan, T. Lacelle, R. Lam, D. Solis, S. Dayanandan, T. Waddell, et al., *Nature Communications* **2023**, *14*, 1 4412.

Table of Contents



Xolography in flow is the first continuous volumetric 3D printing technique based on dual-color photopolymerization. Inside a specifically designed flow cell, enabling homogeneous printing conditions in the constantly flowing resin, objects with true shape and high resolution can continuously be fabricated, bringing the high throughput fabrication of complex-shaped building blocks for tissue engineering into reach.